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(54) Title: ARTICLE HAVING A LOW-FRICTION SURFACE COATING, METHOD OF PREPARING SAID ARTICLE AND COATING COMPOSITION FOR USE IN THE METHOD			
(57) Abstract <p>An article having a two-phase surface coating of low friction when wetted, said coating consisting of polyurethane and poly (N-vinyl lactam), the polyurethane and poly (N-vinyl lactam) each forming a separate phase and the poly (N-vinyl lactam) primarily forming the inner phase of the two-phase structure. In a method of preparing the article a coating composition is applied to the article, said coating composition consisting of polyurethane, poly (N-vinyl lactam) and a solvent system comprising at least two solvents of different volatility, the polyurethane being soluble in at least the mixture of solvents and in the least volatile solvent and the poly (N-vinyl lactam) being soluble in the most volatile solvent but only partly soluble in the least volatile solvent.</p>			
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Article having a low-friction surface coating, method of preparing said article and coating composition for use in the method

5 The present invention relates to an article having a low-friction surface coating when wetted which coating essentially consists of polyurethane without free isocyanate groups and poly (N-vinyl lactam).

10 Particularly but not exclusively the invention relates to plastics articles for medical use and in particular catheters with a low-friction coating of the above mentioned type.

15 The presence of such a low-friction coating on e.g. a catheter provides the catheter with a slippery and lubricating surface when dipped into an aqueous, optionally saline, solution prior to the insertion into a body cavity or when contacted with an aqueous body liquid upon insertion into the body cavity. Thus, the discomfort experienced by the patient when the catheter is inserted into and removed from the body cavity is considerably reduced. The risk of
20 damaging sensitive tissue in connection with the use of the catheter is at the same time considerably reduced.

25 Low-friction coatings based on polyurethane and poly (N-vinyl lactam) are known from i.a. GB patent specification No. 1,600,963 and US patent specifications Nos. 4,666,437 and 4,642,267.

30 The latter US patent specification describes a low-friction polymer blend for use in low-friction coatings for a number of basic materials. The polymer blend essentially consists of an organic, soluble, pre-formed thermoplastic polyurethane without reactive isocyanate groups and a hydrophilic poly (N-vinyl lactam) which blend tolerates the influence of water without loss of the hydrophilic poly (N-vinyl lactam).

35 Furthermore, said patent specification discloses a method of providing the surface of a plastics material with a low-friction coating. In the known method two polymers are dissolved in a mixture of diacetone alcohol and methyl ethyl ketone followed by the evaporation of the solvent after the solution has been applied to

the surface of the plastics article.

The resulting coating is stated to be stable and not to decompose even after prolonged continuous contact with water.

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In some cases said known coating may seem stable when contacted with static water, but in practice it appears that said coating is easily rubbed off the coated plastics article when the article during use is exposed to friction.

10

Coatings prepared as described in the above mentioned US patent specification do not adhere well to the surface of materials which are applied in practice, e.g. softened PVC and polyurethane rubber. Neither do the coatings have a fully satisfactory low-friction effect when located on the surface of the materials of the above mentioned type.

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Attempts have been made to provide a coating of the above mentioned type having an improved low-friction when wetted and at the same time having an improved adherence to e.g. plastics articles compared to known coatings and which can be formed by a simple application method, and surprisingly it has been found that the properties of the coating depend on the inner physical structure of the coating.

20

25 The article of the invention is characterized in that the coating is a two-phase coating, that polyurethane and poly (N-vinyl lactam) each form a separate phase and that poly (N-vinyl lactam) primarily forms the inner phase of the two-phase structure.

30

30 The importance of the special two-phase structure as far as the adherence of the coating to the surface of the coated article is concerned has been confirmed by tests using a coating in which polyurethane forms the discontinuous phase and poly (N-vinyl lactam) forms the continuous phase. These tests have shown that a coating having such a structure does not adhere properly as the coating may be quickly rinsed off in running water.

In most cases the above mentioned two-phase structure exhibits the special property that it is limpid in dry condition and milky white

when wetted and that the milky wetted coating can be converted to a dry limpid coating by drying.

5 The milky appearance in wetted condition is presumably due to the fact that water is absorbed by the discontinuous phase of hydrophilic poly (N-vinyl lactam). The state resulting from such water absorption is stable and reversible and as mentioned above it is possible to produce a dry limpid coating again by drying the wetted coating.

10 This possibility of reversibly changing the coating would appear to be a special characteristic of the coating on the article according to the invention. Thus, investigations of coatings which do not have the above mentioned special two-phase structure have shown that they 15 are milky white already in dry condition and that their appearance does not significantly change when wetted.

20 The above mentioned investigations have shown that in order to obtain said special two-phase structure it is desirable to select specific polyurethanes. Thus, polyurethanes based on e.g. sorbitol and prepared by using trifunctional isocyanates are not suitable for use in the coatings nor are thermoplastic polyurethanes prepared by reacting equivalent amounts of polyether polyols with difunctional diisocyanates.

25 However, surprisingly it has been found that polyurethanes prepared from a polyester polyol and a difunctional isocyanate in which isocyanate is used in an amount equivalent to or less than the equivalent amount in order to avoid free isocyanate groups are 30 suitable for use according to the invention.

Particularly preferred polyurethanes are prepared from polyester polyol based on butane diol and adipic acid.

35 Furthermore, it has been found that the polyurethane should be crystalline i.e. have a crystallinity corresponding to a Shore A hardness of the polyurethane of at least 80. Polyurethanes having a Shore A hardness of above 90 are particularly preferred. Such highly crystalline polyurethanes are particularly suitable in coatings for

articles made from PVC, because said polyurethanes are unaffected by the plastizicers contained in the PVC.

5 Likewise, the polyurethane should have a relatively high molecular weight.

Normally, the molecular weight of commercially available soluble polyurethanes is not stated but the viscosity of a 15% or 20% solution in methyl ethyl ketone is stated instead.

10 The polyurethane contained in the coating should have a molecular weight corresponding to a viscosity of a 15% solution of methyl ethyl ketone of at least 300 cp, and preferably of 500-5000 cp.

15 There seems to be a relationship between crystallinity (Shore A hardness) and molecular weight (solution viscosity) as a higher crystallinity is required at relatively low molecular weights than at high molecular weights. Thus, a relatively low molecular weight may be compensated for by selecting a polyurethane of a higher 20 crystallinity. Vice versa, a polyurethane of a relatively low crystallinity may be chosen provided it has a relatively high molecular weight.

25 The poly (N-vinyl lactam) contained in the coating is preferably polyvinylpyrrolidone and in particular a polyvinylpyrrolidone having a k-value of above approx. 50. Homopolymers of N-vinylbutyrolactam and N-vinylcaprolactam as well as copolymers of N-vinylpyrrolidone, N-vinylbutyrolactam and/or N-vinylcaprolactam are examples of other suitable polymers in the above mentioned group.

30 The coated article is preferably a plastics article or an article having a surface layer of plastics. Preferred plastics are PVC and polyurethane.

35 As mentioned above it is particularly expedient to provide plastics articles for medical use, in particular catheters, such as e.g. urethral catheters, with a low-friction coating when wetted. Other articles, e.g. guide wires, used for inserting catheters into body cavities and comprising a plastics coating may also advantageously

be provided with a coating as described above.

The invention also relates to a method of preparing an article as described above wherein a coating composition comprising a mixture of polyurethane, poly (N-vinyl lactam) and at least two solvents of different volatility is applied to at least a part of the surface of the article, followed by the evaporation of the solvents, the method being characterized in using such a solvent system that the polyurethane is soluble in at least the mixture of solvents and in the least volatile solvent, and that the poly (N-vinyl lactam) is soluble in the most volatile solvent but only partly soluble in the least volatile one.

By using the solvent system as described above poly (N-vinyl lactam) precipitates during the evaporation of solvent while the polyurethane is still dissolved.

In order to expedite the above precipitation a solvent system comprising two mutually miscible solvents is preferably used.

It should be noted that polyurethane and polyvinylpyrrolidone form complexes and that neither of the two phases are pure. Therefore, it is assumed that the phase structure consists of domains which preferably contain polyvinylpyrrolidone, optionally with bordering zones, which mainly consist of a polyvinylpyrrolidone polyurethane complex distributed in a matrix which mainly consists of polyurethane.

The domains of poly (N-vinyl lactam) present in the two-phase structure preferably have a size of about 400 nanometers.

The formation of the two-phase structure is influenced by the ratio of the amount of polyurethane to the amount of poly (N-vinyl lactam). Thus, it appears that the greater the ratio of poly (N-vinyl lactam) to polyurethane is, the greater are the difficulties of causing polyurethane to form the outer (continuous) phase. However, technically speaking, the most interesting coatings are those in which the ratio of poly (N-vinyl lactam) to polyurethane is relatively high. Therefore, a weight ratio of from 1.5:1 - 5:1,

especially 2:1 - 3:1, is preferred, and particularly preferred is a ratio about 2.5:1.

It has also been found expedient to select solvent systems based on
5 the Hansen Solubility Parameters.

The Hansen Solubility Parameters comprise a set of three parameters of a solvent defining the polarity of the solvent, the capability of the solvent to form hydrogen bonds and the dispersion forces. These
10 parameters express the ability of the solvent to mix with other solvents and the ability to dissolve other substances. Polymers may also be described by means of the Hansen Solubility Parameters, and by knowing these parameters it is possible to predict their solubility.

15 The solubility parameters of a number of solvents are disclosed in Allan F.M. Barton: CRC Handbook of Solubility Parameters and Other Cohesion Parameters. CRC Press Inc. Boca, Raton, Florida, 1983.

20 If e.g. methylene chloride is chosen as the solvent in which both polyurethane and polyvinylpyrrolidone are soluble, the other relatively volatile solvent should have an R-value which is higher than or equal to 19, and preferably higher than or equal to 19.5. The above mentioned R-value defines the distance of the solvent from
25 the centre of the solubility sphere of polyvinylpyrrolidone in a three-dimensional space and it is calculated as stated on page 152 of the above reference. Examples of solvents suitable for use together with methylene chloride are acetone (R=21.5), methyl ethyl ketone (R=23.01), ethyl acetate (R=22.6) and tetrahydrofuran (R=21.0). Solvents such as methyl acetate, ethylene carbonate, propylene carbonate, pyridine and butyle acetate are also suitable.
30 It should be noted that ethanol (R=12.7), butyrolacton (R=18.5) and diacetone alcohol (R=18.6) are unsuitable.

35 Surprisingly, the method of the invention has been found suitable for preparing articles for medical use and more particular plastics catheters in a new and economical way.

Catheters having a low-friction coating when wetted are typically

prepared from a long plastics tubing which is cut into pieces of a suitable length. These pieces are then formed into catheter tubings by making the one end pointed and by e.g. attaching a catheter funnel to the catheter by gluing. Finally, the catheters thus prepared are dipped into a liquid coating agent so as to provide them with a low-friction coating.

The surface coating formed by the method of the invention has surprisingly proved to be heat stable and adhesive to such an extent that a tubing provided with such a coating may be converted to medical products e.g. catheters.

Furthermore, the invention relates to a coating composition for use in the method described above. The coating composition comprises a mixture of polyurethane, poly (N-vinyl lactam) and at least two solvents of different volatility and is characterized in that the solvents are selected in such a manner that the polyurethane is soluble in both solvents, and that the poly (N-vinyl lactam) is soluble in the most volatile solvent but only partly soluble in the least volatile solvent.

The invention will now be described in further detail with reference to the following examples:

25 Example 1

Solutions of various polyurethanes (PUR) for use in combination with polyvinylpyrrolidone (PVP) are prepared with the object of providing PVC catheters with a coating.

30 The following standard composition is used:

	<u>Parts by weight</u>	%
35 Polyurethane, 5% in MeCl ₂	83	1.21
MeCl ₂	60	82.12
Acetone	40	12.12
PVP K 90, 10% in MeCl ₂	150	4.55

A solution corresponding to the solution set forth in example 1 of US patent No. 4,642,267 is also prepared. The latter solution is used in example 7 below:

5

Parts by weight

	Diacetone alcohol	75
	Methyl ethyl ketone	25
	PVP (Kollidon 90, BASF)	4
10	Estane 5703 (PUR, B.F. Goodrich)	2

The components are stirred overnight and subsequently the resulting solution is filtered.

- 15 The dipping takes place under identical conditions. Dipping velocity for a tube of 18 cm: 17 sec. Removal time: 46 sec. 3 catheters are dipped into each solution.

Quality grading

20

The quality of the coating is visually graded with regard to the transparency of the film, adherence in dry and wet condition and friction in wet condition.

25

The following grades are used based on the standard deviation of the present tests:

Transparency of film

1. clear
2. slightly turbid (evenly greyish)
3. slightly milky-white
4. unevenly milky-white
5. white

30

Adherence in wet condition

1. adheres under all conditions
2. coating may be rubbed off with difficulty
3. coating may be rubbed off in layers or in spots

35

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4. may be rinsed off in running water

Friction

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1. very low
2. low
3. unchanged compared to PVC
4. high, resisting.

The properties of the coatings are stated in table 1.

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Table 1

Example No	PUR Type	Shore A hardness	Viscosity, cP.	Transparency	Adherence	Friction
1	Irostic 160/38	92	1240 ¹	1	1	1
2	Irostic 160/43	96-97	1240 ¹	1	1	1
3	Irostic 158 C	91-93	710 ¹	1	1	1
4	Irostic 311/27	95	1100 ¹	1	1	1
5	Estane 5703	70-72	180-290 ²	2	3	4
6	Estane 5712-F30	95-98	2800-4000 ²	1	1	1
7	Estane 5703 (US 4,642,267 ex.1)	70-72	180-290 ²	2	3-4	3-4
8	Irostic 300 TN	93-95	80 ¹	3	4	3-4
9	Estane 5711	95	1800-3000 ²	1 ³)	1	1
10	Estane 5720	90	2800-4200 ²	1	2	2

- 1) As a 15% solution in methyl ethyl ketone,
- 2) As a 20% solution in methyl ethyl ketone,
- 3) A few milky white spots possibly due to moisture during evaporation

As will appear from the table the selection of polyurethane has a great influence on the quality of the coating.

It appears from example 7 that the formulation set forth in example 5 of US patent No. 4,642,267 produces a coating of poor adherence and friction.

By comparing the results obtained according to examples 5 and 7 it is apparent that even by using a solvent system which in another 10 context produces a coating of satisfactory properties a poor adherence and friction are obtained. Therefore, the polyurethane in question, Estane 5703, is unsuitable for the intended use. As will appear from the table it has a Shore A hardness of 70-72. This indicates that polyurethanes with a Shore A hardness below 80 are 15 unsuitable.

Example 8 shows that a polyurethane having a too low viscosity (i.e. mole weight) does not adhere satisfactorily.

20 Example 11-28

Two series, A and B, of PUR/PVP solutions are prepared according to the standard procedure of example 1, however, the 40 g of acetone being substituted with a corresponding amount of other solvents as 25 set forth in table 2.

In series A PUR is Irostatic 160/38 from Iromer. Series B uses Estane 5703 from B.F. Goodrich. Irostatic 212K from Iromer is used in example 24. Coated PVC catheters are prepared and they are followed by a 30 grading as to transparency in dry condition and adherence in wet condition.

The results obtained are set forth in table 2.

35 It appears from the table that all the coatings of Series B adhere unsatisfactorily in wet condition. Consequently, it is not possible to improve the result obtained with Estane 5703 by altering the solvent system.

12

The adherence of the coatings of Series A depends on the selection of the least volatile solvent. In case of an R-value of 19.1 or below, Irostatic 160/38 forms a coating of poor adherence. If the R-value is higher a satisfactory adherence and friction are obtained.

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Examples 21 and 22 show that the absence of a solvent to control the precipitation of a separate PVP phase during evaporation causes poor adherence.

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Table 2

Example No.	PUR type ¹⁾	Secondary solvent	Hansen Parameters			Transparency	Adherence
			D H	P H	R ²⁾		
11	A	Tetrahydrofuran	16.8	5.7	8.0	21.0	1
12	B	-0-				2	3
13	A	Pyridine	19.0	8.8	5.9	20.6	2
14	B	-0-				2	4
15	A	Diacetone alcohol	15.8	8.1	10.8	18.6	1
16	B	-0-				1	3
17	A	N-methylpyrrolidone	18.0	12.3	7.2	19.1	2
18	B	-0-				2	3
19	A	Ethyl acetate	15.8	5.3	7.2	22.6	1
20	B	-0-				3	3
21	A	None				1	4
22	B	None				1	4
23	A	Propylene carbonate	20.0	18.0	4.1	21.7	1
24	B	-0-				1	3
25	A	Butyrolactone	19.0	16.6	7.4	18.5	1
26	B	-0-				2	3
27	A	Ethanol	15.8	8.4	19.4	12.7	2
28	B	-0-				2	3
29	Irostic ³⁾	Ethyl acetate	15.8	5.3	7.2	22.6	1
212K							1

- 1) A= Irostatic 160/38
- B= Estane 5703
- 2) Calculated in relation to PVP having (D.P.H.)=(20.6, 14.4, 25.5)
- 3) Irostatic 212K with a Shore A hardness of 95 and a viscosity of 540
5 cp. (15% in MEK).

Example 30

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A standard solution of a polyurethane based on a polyether polyol is prepared (Tecoflex 80A from Thermedics Inc.) and PVC tubes are coated by dipping in the solution and are dried.

15

After drying the coating is uniform and has a dull surface. When wetted it becomes slippery but adheres very poorly and after about 10 sec. in running water the coating is rinsed off.

Example 31

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The friction of a number of catheters in wet condition is measured by means of an apparatus consisting of a fixed support with a horizontal surface onto which a sliding zone is attached consisting of a medical lambskin having the dimensions 1.5 x 3.0 cm.

25

A metal block having an underside which is provided with two transverse grooves with two short pieces of catheters mounted in said grooves may be drawn longitudinally of said sliding zone. The block is connected with a pull device which produces a horizontal force which increases by 25 g/min. The block weighs 70 g. When measuring, the catheter pieces and the lambskin are wetted and the block is placed at one end of the sliding zone.

The load is increased until the block begins to move. The load at the point of movement defines the friction.

The following results were obtained.

15

Coatings according to the invention:

	<u>Example No.</u>	<u>Pull force in grammes</u>
5	1	19.1
	2	17.5
	6	16.7
	9	14.5
	29	15.6

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Comparative examples:

	<u>Example No.</u>	<u>Pull force in grammes</u>
15	5	>38.9 (the block tips over)
	7	34.1
	20	27.3

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CLAIMS

1. An article having a low-friction surface coating when wetted which coating essentially consists of polyurethane without free isocyanate groups and poly (N-vinyl lactam), characterized in that the coating is two-phased, that polyurethane and poly (N-vinyl lactam) each form a separate phase and that poly (N-vinyl lactam) primarily forms the inner phase of the two-phase structure.
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- 10
2. An article according to claim 1, characterized in that the polyurethane is prepared from a polyester polyol and a difunctional isocyanate.
- 15
3. An article according to claim 2, characterized in that the polyurethane is prepared from a polyester polyol obtained by reacting butane diol with adipic acid.
- 20
4. An article according to any of the preceding claims, characterized in that the polyurethane has a crystallinity corresponding to a Shore A hardness of at least 80.
- 25
5. An article according to any of the preceding claims, characterized in that the molecular weight of the polyurethane corresponds to a viscosity of a 15% solution of polyurethane in methyl ethyl ketone of at least 300 cp.
- 30
6. An article according to claim 5, characterized in that the molecular weight of the polyurethane corresponds to a viscosity of from 500 to 5000 cp.
- 35
7. An article according to any of the preceding claims, characterized in that the poly (N-vinyl lactam) is polyvinyl-pyrrolidone, a homopolymer of N-vinylbutyrolactam or N-vinyl-caprolactam or a copolymer of N-vinylpyrrolidone, N-vinyl-butyrolactam and/or N-vinylcaprolactam.
8. An article according to any of the preceding claims, characterized in that the article is a plastics article for

medical use.

9. An article according to claim 8, characterized in that the article is a plastics catheter.

5

10. A method of preparing an article according to claim 1 wherein a coating consisting of a mixture of polyurethane, poly (N-vinyl lactam) and at least two solvents of different volatility are applied to at least part of the surface of the article followed by evaporation of the solvents, characterized in using a solvent system such that the polyurethane is soluble in at least the mixture of solvents and in the least volatile solvent, and that the poly (N-vinyl lactam) is soluble in the most volatile solvent and only partly soluble in the least volatile solvent.

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11. A method according to claim 10, characterized in using two solvents which are miscible.

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12. A method according to claims 10 or 11, characterized in using poly (N-vinyl lactam) and polyurethane in a ratio of 1.5:1 - 5:1, preferably of 2:1 - 3:1.

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13. A method according to any of the claims 10-12 wherein the poly (N-vinyl lactam) is polyvinylpyrrolidone, characterized in that the least volatile solvent has an R-value of at least 19, preferably at least 19.5 relative to polyvinylpyrrolidone.

30

14. A method according to any of the claims 10-13, characterized in that the most volatile solvent is methylene chloride and that the least volatile solvent is selected from a group consisting of acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, ethylene carbonate, propylene carbonate, pyridine, butyl acetate and tetrahydrofuran.

35

15. A method according to any of the claims 10-14, characterized in forming a coating on the article before it is converted into its final form.

16. A method according to claim 15 for providing a surface coating

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on a catheter, characterized in forming a coating on a catheter tubing, cutting said tubing into pieces and converting the resulting pieces into catheters.

- 5 17. A coating composition for use in the method according to any of the claims 10-16 and comprising a mixture of polyurethane, poly (N-vinyl lactam) and at least two solvents of different volatility, characterized in that the solvents have been selected in such a manner that the polyurethane is soluble in both solvents
10 and that the poly (N-vinyl lactam) is soluble in the most volatile solvent but only partly soluble in the least volatile solvent.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 89/00255

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC5: C 08 J 7/04, A 61 L 29/00, B 05 D 5/08

II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
IPC5	A 61 L; B 05 D; C 08 J
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *	

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages ***	Relevant to Claim No. ***
X,P	US, A, 4835003 (BECKER ET AL) 30 May 1989, see abstract; claim 1 --	1,7-9
A	US, A, 4642267 (CREASY ET AL) 10 February 1987, see abstract -----	1

* Special categories of cited documents: 10

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IV. CERTIFICATION

Date of the Actual Completion of the International Search
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Barbro Nilsson *Barbro Nilsson*

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4835003	30/05/89	NONE	
US-A- 4642267	10/02/87	NONE	

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